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Ruthenium complexes of hexakis(cyanophenyl)[3]radialenes and their di(cyanophenyl)methane precursors: synthesis, photophysical and electrochemical properties

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Abstract

The coordination chemistry of cross-conjugated ligands and the effect of cross-conjugation on the nature of metal-metal and metal-ligand interactions have received limited attention. To explore the effects of cross-conjugation eight ruthenium complexes were synthesised, namely mononuclear complexes of two isomeric cross-conjugated [3]radialenes [RuCp(PPh_3)$_2$(**L**)]PF_6 and [{RuCp*(dppe)}(**L**)]PF_6 (L = hexakis(4-cyanophenyl)[3]radialene, **2**; hexakis(3-cyanophenyl)[3]radialene, **3**), and dinuclear complexes [{RuCp(PPh_3)$_2$}$_2$(**L**)](PF_6)$_2$ and [{RuCp*(dppe)}$_2$(**L**)](PF_6)$_2$ of the diarylmethane precursors (L = 4,4'-dicyanodiphenylmethane, **4**; 3,3'-dicyanodiphenylmethane, **5**) of the [3]radialenes. Considerable synthetic challenges allowed only clean isolation of mononuclear complexes of the multidentate radialenes **2** and **3**. As expected, coordinating a positively charged metal induces a red shift for the π-π* transition in complexes of ligand **2**, but unexpectedly a blue shift for the same transition in complexes of **3** was observed. This points to notable conformational differences for the [3]radialene in the ruthenium complexes of the *para*- (**2**) versus *meta*- (**3**) substituted hexaaryl[3]radialenes. Cyclic voltammetry indicates that the methylene spacer in **4** and **5** does not enable any interaction between metal centres and the absorption behaviour is essentially as observed for [Ru(NCPh)(PPh_3)$_2$Cp]PF_6 and [Ru(NCPh)(dppe)Cp*]PF_6 but generally with a slight red shift in absorbance maxima.

Keywords: Ruthenium complexes; [3]radialenes; nitrile donors; fluorescence; cyclic voltammetry

1. Introduction

Ruthenium(II) complexes of polypyridyl ligands with the ability to bridge multiple metals have been extensively studied [1, 2], for example in the context of light harvesting antennae [3], to study electron transfer processes [4, 5] and for molecular electronics [6, 7]. Multinuclear complexes of linearly conjugated ligands exhibit interesting photophysical and electrochemical properties that, dependent on the nature of the bridging ligand [8, 9], often possess the ability to facilitate metal-metal interactions through their conjugated bridges. Carbon-based molecular wires also show excellent metal-metal interactions over quite large distances [10, 11] that are again facilitated through their linearly π-conjugated systems. In contrast, the nature of metal-metal and metal-ligand interactions that result from other modes of π-electron communication, in particular cross-conjugation [12], have received limited attention [13, 14].

Radialenes are cross-conjugated molecules, with the general formula $C_{2n}H_{2n}$ (figure 1a), that possess *n* ring atoms and *n* exocyclic double bonds [12, 15, 16, 17]. A straightforward method of accessing stable hexaaryl[3]radialenes, using Fukunaga's method of reacting stabilized carbanions with tetrachlorocyclopropene [18, 19], was first reported by Oda [20, 21]. As a consequence, this advance led to an increase in the availability of [3]radialene derivatives, including compounds able to coordinate transition metals, such as hexa(2-pyridyl)[3]radialene (**1**) (figure 1b) [22, 23] and hexakis(4-cyanophenyl)[3]radialene (**2**) (figure 1c) [20, 21]. These compounds possess six metal binding sites and have the potential to be involved in bridging multiple metal centres through their unique cross-conjugated scaffold.

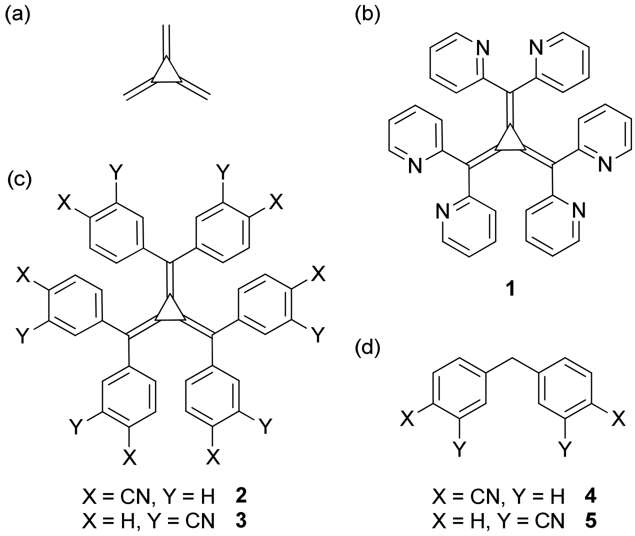


Figure 1. The structures of (a) [3]-radialene, (b) hexa(2-pyridyl)[3]radialene (**1**); (c) hexakis(4-cyanophenyl)[3]radialene (**2**) and hexakis(3-cyanophenyl)[3]radialene (**3**); and (d) 4,4'-dicyanodiphenylmethane (**4**) and 3,3'-dicyanodiphenylmethane (**5**).

The coordination chemistry of hexaaryl- and hexa-heteroaryl[3]radialenes has been studied to a limited extent [23-27]. Two isomers (*rac* and *meso*) of a dinuclear bis(2,2'-bipyridyl)ruthenium(II) complex incorporating **1** have also been reported [28], although no metal-metal interactions were observed. The present contribution details the synthesis and spectroscopic properties of the first ruthenium(II) complexes of ligand **2** and its isomer hexakis(3-cyanophenyl)[3]radialene (**3**) (figure 1c), as well as investigations into the dinuclear complexes of the diaryl methane precursors, 4,4'-dicyanodiphenylmethane (**4**) and 3,3'-dicyanodiphenylmethane (**5**) (figure 1d).

2. Experimental section

2.1 *General procedures*

Melting points were determined using a Gallenkamp variable heat melting point apparatus and are uncorrected. UV-visible absorption spectra were recorded on a Varian CARY 5000 spectrophotometer. Samples were dissolved in dichloromethane at a concentration of approximately 0.03 mM. Fluorescence spectra were recorded on a Varian CARY Eclipse spectrophotometer. Samples were dissolved in dichloromethane at a concentration of approximately 0.01 mM. Infrared spectra were recorded using a Perkin Elmer Spectrum 100 FT-IR spectrometer with universal ATR sampling accessory. The Campbell microanalytical laboratory at the University of Otago performed elemental analyses.

High resolution electrospray ionisation mass spectroscopy (ESI-HRMS) was performed by the Adelaide Proteomics Centre using an LTQ Orbitrap XL ETD spectrometer. Samples were dissolved in HPLC grade acetonitrile or methanol at a concentration of 0.01 mg/cm^3. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. ^{1}H NMR spectra recorded in $CDCl_3$ were referenced to the internal standard Me_4Si, 0 ppm. ^{31}P{^{1}H} NMR spectra were recorded in $CDCl_3$ and referenced to external H_3PO_4. Unless otherwise stated, reagents were obtained from commercial sources and used as received. 4,4′-Dicyanodiphenylmethane (**4**) [26], 3,3'-dicyanodiphenylmethane (**5**) [29], hexakis(4-cyanophenyl)[3]radialene (**2**) [21], hexakis(3-cyanophenyl)[3]radialene (**3**) [29], $RuCp(PPh_3)_2Cl$ [30], and RuCp*(dppe)Cl [31] were synthesised via literature procedures.

2.2 *X-Ray crystallography*

A crystal of **11** was mounted under oil on a nylon loop and X-ray diffraction data collected at 150 K with synchrotron radiation (λ = 0.7107 Å) using the Macromolecular Crystallography beamline (MX1) at the Australian Synchrotron [32]. The data set was corrected for absorption using a multi-scan method, and structures were solved by direct methods using SHELXS-97 [33] and refined by full-matrix least squares on *F*2 by SHELXL-97 [34], interfaced through the program X-Seed [35]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. CCDC 939490 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.2.1 Crystal data for 11. $C_{44}H_{45}N_1Ru_1P_3F_6Cl_1$, FW = 931.24, monoclinic, $P2_1/n$, a = 11.715(2), b = 17.841(4), c = 20.23(4) Å, β = 93.549(3), V = 4220.1(15) Å^3, Z = 4, ρ = 1.466 Mg cm^{-3}, μ = 0.608 mm^{-1}, $F(000)$ = 1904, yellow rod, 0.28 × 0.19 × 0.14 mm, 2θmax = 57.76°, T = 150(2) K, 73124 reflections, 10691 unique (96.4% completeness), Rint = 0.0459, 580 parameters, GOF = 1.032, $wR2$ = 0.1649 for all data, $R1$ = 0.0587 for 9753 data with $I > 2\sigma(I)$.

2.3 *Synthesis of ruthenium complexes*

2.3.1 General synthesis of [{RuCp(PPh$_3$)$_2$}$_n$(L)](PF$_6$)$_n$ complexes. Ligand, RuCp(PPh$_3$)$_2$Cl (1 or 2 equiv.) and NH_4PF_6 (4+ equiv.) in dichloromethane (10 mL) was heated at reflux for 3h or overnight. The resultant mixture was cooled to room temperature and methanol (10 mL) was added. The dichloromethane was removed under reduced pressure and the suspension cooled to 4°C overnight. The precipitate was isolated and air dried.

*2.3.1.1. [{RuCp(PPh$_3$)$_2$}$_2$(**4**)](PF$_6$)$_2$ (**6**).* Compound **4** (20.0 mg, 91.6 μmol), RuCp(PPh$_3$)$_2$Cl (133 mg, 183 μmol) and NH_4PF_6 (59.7 mg, 366 μmol) were treated as described to yield **6** as a yellow solid (137 mg, 74%). Mp: 142-145°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.01 (s, 2H, CH_2), 4.53 (s, 10H, Cp), 7.07-7.41 (m, 68H, Ar); ^{31}P{^{1}H} NMR (121

MHz, $CDCl_3$): δ 40.79 (s, PPh_3), -144.58 (septet, *J* = 712 Hz, PF_6); HRMS (*m/z*): ($[M-PF_6^-]^+$) calcd for $C_{97}H_{80}N_2Ru_2P_5F_6$, 1745.30412; found 1745.30633; FT-IR: v_{max}/cm^{-1} 2226 (C≡N), 839 (PF_6); Anal. calcd for $C_{97}H_{80}N_2Ru_2P_6F_{12}$ C 61.65, H 4.27, N 1.48; found, C 61.45, H 4.39, N 1.53%.

*2.3.1.2. [{RuCp(PPh$_3$)$_2$}$_2$(**5**)](PF$_6$)$_2$ (**7**).* Compound **5** (20.0 mg, 91.6 μmol), $RuCp(PPh_3)_2Cl$ (133 mg, 183 μmol) and NH_4PF_6 (59.7 mg, 366 μmol) were treated as described to yield **7** as a yellow solid (143 mg, 83%). Mp: 157-159°C; ^1H NMR (300 MHz, $CDCl_3$): δ 4.01 (s, 2H, CH_2), 4.58 (s, 10H, Cp), 6.70 (d, 2H, *J* = 9.0 Hz, ligand Ar), 7.08-7.37 (m, 62H, Ar), 7.46 (d, 2H, *J* = 9.0 Hz, ligand Ar), 7.66 (s, 2H, ligand Ar); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 41.00 (s, PPh_3), -144.73 (septet, *J* = 713 Hz PF_6); HRMS (*m/z*): ($[M-PF_6^-]^+$) calcd for $C_{97}H_{80}N_2Ru_2P_5F_6$, 1745.30412; found 1745.30517; FT-IR: v_{max}/cm^{-1} 2229 (C≡N), 833 (PF_6); Anal. calcd for $C_{97}H_{80}N_2Ru_2P_6F_{12}\cdot½(CH_2Cl_2)$ C 60.61, H 4.23, N 1.45; found, C 60.87, H 4.13, N 1.79%.

*2.3.1.3. [RuCp(PPh$_3$)$_2$(**2**)]PF$_6$ (**8**).* Compound **2** (25.0 mg, 36.5 μmol), $RuCp(PPh_3)_2Cl$ (26.5 mg, 36.5 μmol) and NH_4PF_6 (11.9 mg, 73.0 μmol) in methanol (15 mL) was heated at reflux overnight. The dark red solution was cooled to 4°C overnight and the resultant precipitate was isolated and air dried to yield **8** as a red solid (31 mg, 62%). Mp: 205-207 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 4.66 (s, 5H, Cp), 6.90 (m, 4H, Ar), 7.03-7.44 (m, 50H, Ar); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 39.56 (m, PPh_3), 39.69 (m, PPh_3), -145.72 (septet, *J* = 711 Hz, PF_6); HRMS (*m/z*): ($[M-PF_6^-]^+$) calcd for $C_{89}H_{59}N_6Ru_1P_2$, 1375.33145; found 1375.33711; FT-IR: v_{max}/cm^{-1} 2227 (C≡N), 830 (PF_6); Anal. calcd for $C_{89}H_{59}N_6Ru_1P_3F_6\cdot1½(CH_2Cl_2)$ C 65.69, H 3.80, N 5.10; found, C 66.02, H 4.01, N 4.48%.

*2.3.1.4. [RuCp(PPh$_3$)$_2$(**3**)]PF$_6$ (**9**).* Compound **3** (5.0 mg, 7.3 μmol), RuCp(PPh$_3$)$_2$Cl (5.3 mg, 7.3 μmol) and NH$_4$PF$_6$ (2.4 mg, 14.6 μmol) in dichloromethane (5 mL) were treated as described (only 5 mL of methanol added) to yield **9** as an orange solid (7.6 mg, 76%). Mp: 200-204°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.58 (s, 5H, Cp), 6.62-7.79 (m, 54H, Ar); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 40.95 (s, PPh$_3$), -144.59 (septet, *J* = 710 Hz, PF$_6$); HRMS (*m/z*): ([M-PF$_6^-$]$^+$) calcd for C$_{89}$H$_{59}$N$_6$Ru$_1$P$_2$, 1375.33145; found 1375.33637; FT-IR: ν_{max}/cm^{-1} 2231 (C≡N), 836 (PF$_6$).

2.3.2 General synthesis of [{RuCp*(dppe)}$_n$(L)](PF$_6$)$_n$ complexes. Ligand, RuCp*(dppe)Cl (1 or 2 equiv.) and NH$_4$PF$_6$ (4+ equiv.) in dichloromethane (10 mL) was heated at reflux overnight. The resultant mixture was cooled to room temperature, the solvent reduced to *ca.* 1 mL and methanol (10 mL) was added. The dichloromethane was removed under reduced pressure and the suspension cooled to 4°C overnight. The precipitate was isolated and air dried.

*2.3.2.1 [{RuCp*(dppe)}$_2$(**4**)](PF$_6$)$_2$ (**10**).* Treatment of compound **4** (5.0 mg, 23 μmol), RuCp*(dppe)Cl (28.0 mg, 46 μmol) and NH$_4$PF$_6$ (15 mg, 92 μmol) as described yielded **10** as a yellow solid (31 mg, 76%). Mp: 207-210°C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.49 (s, 30H, Cp*), 2.34-2.56 (m, 8H, 4×CH$_2$) 3.88 (s, 2H, CH$_2$), 6.50 (d, 4H, *J* = 8.2 Hz, ligand Ar), 7.11 (d, 4H, *J* = 8.2 Hz, ligand Ar), 7.46-7.54 (m, 40H, Ar); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 74.06 (s, dppe), -144.78 (septet, *J* = 712 Hz, PF$_6$); HRMS (*m/z*): ([M-PF$_6^-$]$^+$) calcd for C$_{87}$H$_{88}$N$_2$Ru$_2$P$_5$F$_6$, 1633.36672; found 1633.36709; FT-IR: ν_{max}/cm^{-1} 2227 (C≡N), 835 (PF$_6$); Anal. calcd for C$_{87}$H$_{88}$N$_2$Ru$_2$P$_6$F$_{12}$ C 58.78, H 4.99, N 1.58; found, C 58.55, H 4.89, N 1.64%.

*2.3.2.2 [{RuCp*(dppe)}$_2$(**5**)](PF$_6$)$_2$ (**11**).* Compound **5** (5.0 mg, 23 μmol), RuCp*(dppe)Cl (28.0 mg, 46 μmol) and NH_4PF_6 (15 mg, 92 μmol) were treated as described to give **11** as a yellow solid (25 mg, 62%) with a small number of crystals suitable for X-ray crystallography recovered. Mp: 232-235°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (s, 30H, Cp*), 2.39-2.59 (m, 8H, 4×CH_2), 3.77 (s, 2H, CH_2), 6.42-6.47 (m, 4H, Ar), 7.07-7.63 (m, 44H, Ar); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 74.09 (s, dppe), -144.79 (septet, J = 711 Hz, PF_6); HRMS (*m/z*): ([M-PF_6^-]$^+$) calcd for $C_{87}H_{88}N_2Ru_2P_5F_6$, 1633.36672; found 1633.37059; FT-IR: ν_{max}/cm^{-1} 2229 (C≡N), 833 (PF_6); Anal. calcd for $C_{87}H_{88}N_2Ru_2P_6F_{12}$·$CH_2Cl_2$ C 57.03, H 4.84, N 1.49; found, C 57.48, H 4.99, N 1.78%.

*2.3.2.3. [{RuCp*(dppe)}(**2**)]PF$_6$ (**12**).* Compound **2** (20.0 mg, 29.2 μmol), RuCp*(dppe)Cl (18.0 mg, 29.2 μmol) and NH_4PF_6 (9.6 mg, 58.4 μmol) were treated as described to yield **12** as a purple solid (30 mg, 78%). Mp: 239°C dec.; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (s, 15H, Cp*), 2.25-2.81 (m, 4H, 2×CH_2), 6.09-6.14 (m, 2H, Ar), 6.81-6.97 (m, 9H, Ar), 7.14-7.25 (m, 13H, Ar), 7.43-7.68 (m, 20H, Ar); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 74.01 (s, dppe), -145.12 (septet, J = 713 Hz, PF_6); HRMS (*m/z*): ([M-PF_6^-]$^+$) calcd for $C_{84}H_{63}N_6RuP_2$, 1319.36275; found 1319.37170; FT-IR: ν_{max}/cm^{-1} 2227 (C≡N), 830 (PF_6); Anal. calcd for $C_{84}H_{63}N_6RuP_3F_6$·CH_2Cl_2 C 65.89, H 4.23, N 5.42; found, C 66.12, H 4.29, N 5.08%.

*2.3.2.4. [{RuCp*(dppe)}(**3**)]PF$_6$ (**13**).* Compound **3** (10 mg, 16 μmol), RuCp*(dppe)Cl (9.0 mg, 16 μmol) and NH_4PF_6 (4.8 mg, 29 μmol) in dichloromethane (5 mL) were treated as described (5 mL of methanol used) to yield **13** as an orange solid (14 mg, 71%). Mp: 187-190°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (s, 15H, Cp*), 2.23-2.65 (m, 4H, 2×CH_2), 7.14-7.72 (m, 44H, Ar); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 74.42 (s, dppe), -145.06 (septet, J = 712 Hz, PF_6); HRMS (*m/z*): ([M-PF_6^-]$^+$) calcd for $C_{84}H_{63}N_6RuP_2$, 1319.36275; found

1319.37107; FT-IR: ν_{max}/cm^{-1} 2229 (C≡N), 836 (PF_6); Anal. calcd for $C_{84}H_{63}N_6RuP_3F_6{\cdot}CH_2Cl_2$ C 65.89, H 4.23, N 5.42; found, C 65.73, H 4.50, N 5.03%.

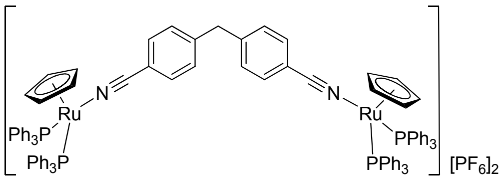
2.3 *Cyclic voltammetry*

Cyclic voltammetry measurements on **6**, **7**, **10** and **11** were performed on a PAR Model 263A potentiostat under nitrogen. Measurements were recorded on 1 mM solutions in dichloromethane/0.1 M [(n-$C_4H_9)_4$]NPF_6] solution using a platinum working electrode, and platinum wire auxiliary and pseudo-reference electrodes. Ferrocene was added as an internal standard on completion of each experiment and tabulated potentials are given *vs* the saturated calomel electrode [$E_0(Fc/Fc^+)$ = +0.46 V *vs* SCE (dichloromethane)]. Cyclic voltammetry was performed with a sweep rate of 100 mVs^{-1}. Complexes **8**, **9**, **12** and **13** were not stable in the presence of supporting electrolyte.

3. Results and discussion

3.1 Synthesis

Eight discrete ruthenium complexes (**6-13**) were synthesised (chart 1). Based on the synthesis of related compounds by Bruce [36] and Low [37], treatment of **4** and **5** with two equivalents of $RuCp(PPh_3)_2Cl$ and ammonium hexafluorophosphate in dichloromethane led to the formation of the expected dinuclear complexes **6** and **7** in good yield. Characteristic peaks for the cyclopentadienyl ligand (δ 4.53 for **6**, 4.58 for **7**) and triphenylphosphine ligands (δ 40.79 for **6**, 41.00 for **7**) were seen in the ^1H and $^{31}P\{^1H\}$ NMR spectra, respectively (table 1). The PF_6 counterion was also observed in the $^{31}P\{^1H\}$ NMR spectra at δ -144.58 (J_{PF} = 712 Hz) for **6** and -144.73 (J_{PF} = 713 Hz) for **7**, while the methylene spacers of the ligands **4** and **5** were accounted for with integrals in the correct ratio for the formation of the expected dinuclear products. The IR spectra showed strong nitrile absorption bands at 2226 and 2229 cm^{-1} for **6** and **7** respectively, compared with the free ligands at 2225 and 2224 cm^{-1} (table 1). High resolution mass spectrometry and elemental analysis further confirmed the identity and purity of the complexes.



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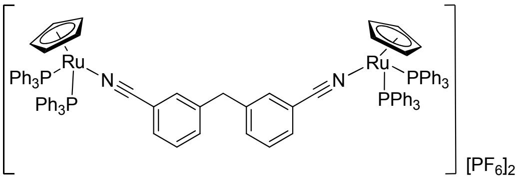

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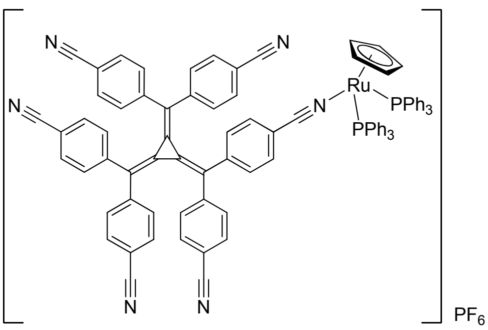

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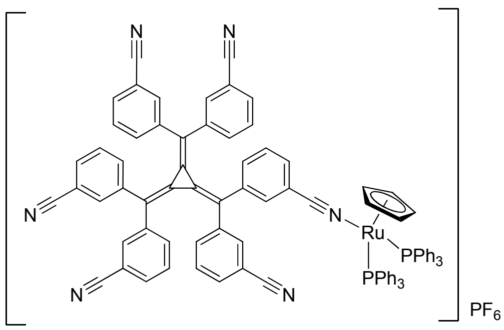

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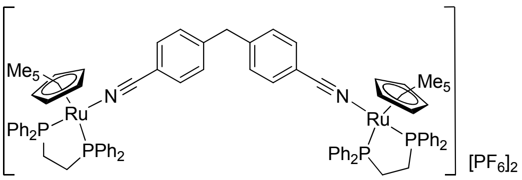

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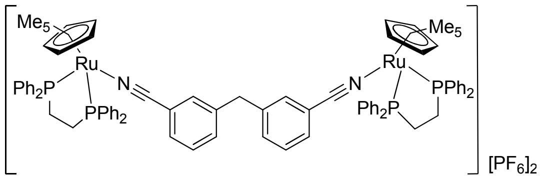

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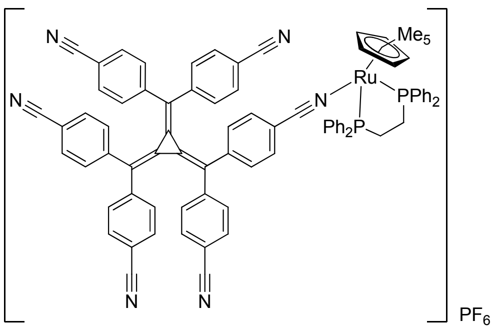

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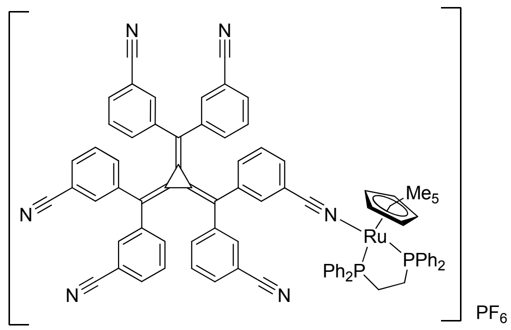

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Chart 1. Ruthenium complexes synthesised in this study.

Table 1. Selected spectroscopic data for compounds **2-13**.

Compound	$\nu_{C\equiv N}$ /cm^{-1}	$\nu_{P\text{-}F}$ /cm^{-1}	Cp δ_H /ppm	Cp* δ_H /ppm	CH_2 δ_H /ppm	PR_3 δ_P /ppm
2	2224					
3	2228					
4	2225				4.10	
5	2224				4.05	
6	2226	839	4.53		4.01	40.79
7	2229	833	4.58		4.01	41.00
8	2227	830	4.66			39.56, 39.69
9	2231	836	4.58			40.95
10	2227	835		1.49	3.88	74.06
11	2229	833		1.51	3.77	74.09
12	2227	830		1.51		74.01
13	2229	836		1.49		74.42

The synthesis of $RuCp(PPh_3)_2$ complexes of the radialene ligands was more challenging. For reactions involving either **2** or **3**, multiple products were observed when high M:L ratios (between 2:1 and 5:1) were used. The products of these reactions were identified as a mixture of species in the case of **2**, specifically a mononuclear complex **8** and three different isomers of a dinuclear complex by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, and mass spectrometry. As well as observing the mixture of dinuclear complexes (*m/z* = 2211.7) and the mononuclear complex (*m/z* = 1375.5) in the mass spectrum, a third peak was seen at *m/z* 1112.8. This last peak likely corresponds to the loss of one triphenylphosphine ligand from complex **8** and possibly chelation of **2** to the single metal centre. Such a coordination mode has been observed in 2-D coordination polymers formed with silver(I) and **2** [26]. In this case however the compound forms in the mass spectrum and was not confirmed to be present in the product mixture.

The synthesis of the mononuclear complex **8** in 62% yield was accomplished by reaction of **2** with only one equivalent of $RuCp(PPh_3)_2Cl$ and heating at reflux overnight. The ^1H NMR spectrum revealed a single characteristic peak for the cyclopentadienyl ligand (δ 4.66) and elemental analysis indicated the product was pure **8**. The $^{31}P\{^1H\}$ NMR spectrum exhibits two peaks at δ 39.56 and 39.69 which were assigned to the two triphenylphosphine ligands of **8** due to restricted rotation around the Ru-N≡C bond in the complex (ESI, Figure SI 5). This restricted rotation is due to the considerable combined steric bulk of the ligand, **2**, and the triphenylphosphine ligands. In a concerted effort to form the chelated by-product observed in the mass spectrum, copper(I) iodide was added to the reaction to promote the loss of triphenylphosphine [38] and subsequent chelation. Thus heating **2**, $RuCp(PPh_3)_2Cl$ and copper iodide (1:1:2 ratio) in methanol at reflux for three days lead only to a poorly soluble purple precipitate that was not analysed further.

Following the synthesis conditions used for **8**, reaction of **3** with one equivalent of $RuCp(PPh_3)_2Cl$, heating at reflux overnight, gave **9** in 76% yield. The ^1H and $^{31}P\{^1H\}$ NMR spectrum of **9** is similar to that of **8** (table 1). Only one signal is observed in the $^{31}P\{^1H\}$ NMR, indicating that the two triphenylphosphine groups are equivalent and thus that free rotation around the ruthenium centre can occur consistent with the more divergent arrangement of nitrile donors in **3**. HRMS confirmed the formation of **9** which gives a molecular ion $[\mathbf{9}\text{-}PF_6]^+$ at *m/z* 1375.33637 (calc. *m/z* 1375.33145). In a similar manner to **8**, compound **9** also loses a PPh_3 ligand in the mass spectrometer. Furthermore, pure samples of the dinuclear complexes of **3** could not be isolated from reactions using higher M:L ratios and so only the mononuclear Ru complexes of the radialene ligands **2** and **3** were available for further study.

To eliminate the possibility of chelation in the synthesis of monodentate hexaaryl[3]radialene monoruthenium species, RuCp*(dppe)Cl was used instead of

$RuCp(PPh_3)_2Cl$. As reported {[39] and references therein}, this chelating phosphine is difficult to displace and thus strictly only one nitrile group can be accommodated within its coordination sphere. Treatment of the two diaryl compounds, **4** and **5**, with two equivalents of RuCp*(dppe)Cl and NH_4PF_6 in dichloromethane gave dinuclear complexes **10** and **11** respectively. Characteristic peaks for the pentamethyl-cyclopentadienyl (Cp*) and 1,2-bis(diphenylphosphino)ethane (dppe) ligands were seen in the ^1H and $^{31}P\{^1H\}$ NMR spectra respectively (table 1). The methylene spacers of the ligands **4** and **5** were also observed with integrals in the correct ratio for the formation of the expected dinuclear products. Further evidence for **10** and **11** was provided by the FT-IR spectra which revealed strong nitrile absorption bands at 2227 and 2229 cm^{-1} for **4** and **5** respectively.

Synthesis of the equivalent RuCp*(dppe) complexes of both **2** and **3**, complexes **12** and **13** respectively, proved straightforward and the compounds were isolated in good yields of 71 and 78%. Characteristic peaks for the Cp* and dppe ligands were seen in the ^1H and $^{31}P\{^1H\}$ NMR spectra, and the PF_6 counterion was also observed in the $^{31}P\{^1H\}$ NMR spectra at δ -145.12 (J_{PF} = 713 Hz) for **12** and -145.06 (J_{PF} = 712 Hz) for **13**. The IR spectra confirmed the presence of strong nitrile absorption bands at 2227 and 2229 cm^{-1} for **12** and **13** respectively, consistent with coordination to ruthenium. As only one $^{31}P\{^1H\}$ NMR signal was observed for both of these complexes it is apparent that free rotation around the ruthenium centre can occur (compared with **8**), which is consistent with observations of the Tolman cone angles for the co-ligands [40, 41] and the structures of [3]radialenes **2** and **3**.

3.2 Crystal Structure of 11

A small number of yellow rod-shaped crystals of **11** suitable for X-ray crystallography were selected from the microcrystalline precipitate isolated directly from the reaction. The dinuclear complex (figure 2) crystallises in the monoclinic space group $P2_1/n$ with an asymmetric unit that contains half a molecule of **5**, a RuCp*(dppe) moiety, one hexafluorophosphate anion, and one half occupied dichloromethane solvate molecule. The structure was refined with significant disorder of the ligand (disordered over two positions with *ca.* 65:35 occupancy) and the dichloromethane solvate molecule. The bond lengths and angles of **11** around the ruthenium(II) centre are comparable to a benzonitrile complex [Ru(NCPh)(dppe)Cp*]PF_6 (table 2), the structure of which was previously reported by Low [37]. One phenyl ring of **5** is involved in weak face-to-face π-stacking with the dppe ligand of one ruthenium metal centre (phenyl ring centroid-to-centroid distance of 4.071 Å) whilst the second is involved in edge-to-face stacking with the dppe ligand of the other ruthenium atom (phenyl ring centroid-to-centroid distance of 4.699 Å).

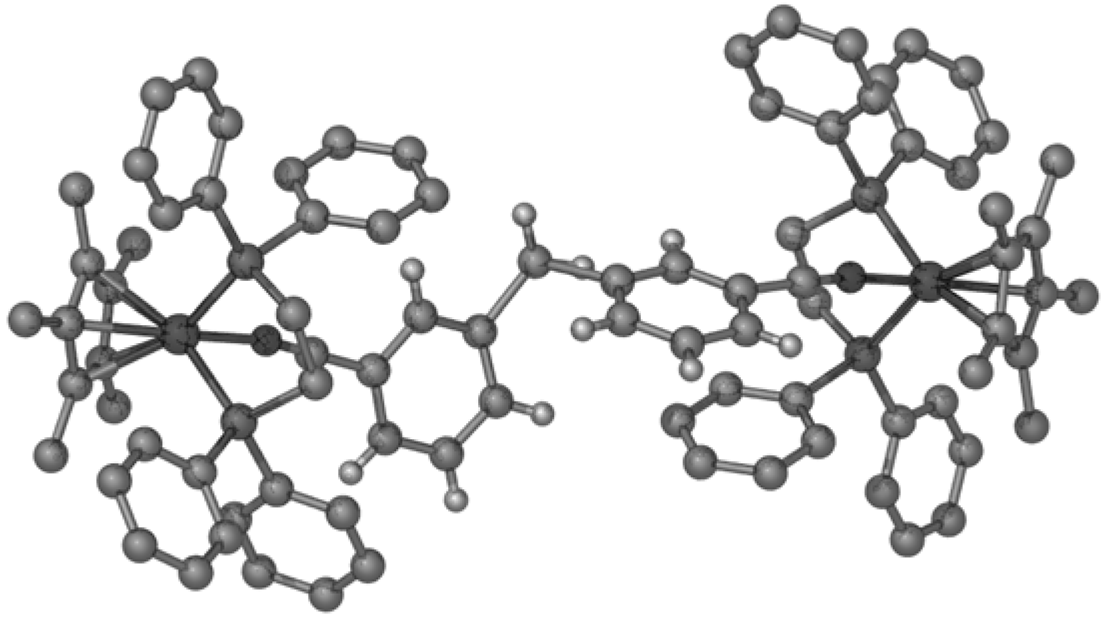

Figure 2. A perspective view of the dinuclear complex **11**. Hydrogen atoms (except those on the ligand), anions and solvate molecules have been omitted. For colour images of **11** see ESI, Figures S6 and S7.

Table 2. Selected bond lengths (Å) and angles (°) for **11** and [Ru(NCPh)(dppe)Cp*]PF_6. The average bonds lengths of the disorder model of **5** have been quoted.

Compound	Ru-N	C≡N	Ru-P(1)	Ru-P(2)	P-Ru-P	Ru-N≡C
11	2.034(7)	1.141(13)	2.306(1)	2.312(1)	83.65(3)	172.5(17)
[Ru(NCPh)(dppe)Cp*]PF_6[a]	2.027(5)	1.146(7)	2.315(1)	2.315(1)	83.50(5)	173.6(4)

[a] Ref. [37]

3.3 Photophysical and Electrochemical Properties

UV-visible absorption and fluorescence spectra for each of the complexes were recorded in dichloromethane (table 3). The absorption maxima for **6** and **7**, 324 and 315 nm respectively, are fairly consistent with that of [Ru(NCPh)$(PPh_3)_2$Cp]PF_6, 307 nm, with a slight red shift observed. For [Ru(NCPh)$(PPh_3)_2$Cp]PF_6 this band has previously been attributed as an overlapping of the $Ru_{d\pi}$-Cp MLCT and $Ru_{d\pi}$-$NCR_{\pi*}$ MLCT transitions [37]. In [Ru(NCPh)(dppe)Cp*]PF_6 these two transitions can be differentiated as absorption maxima at 310 and 346 nm [37] and can be observed in complexes **10** and **11** as absorption maxima at 321 and 309 nm with shoulders at 347 and 343 nm respectively.

Table 3. Photophysical properties of the ruthenium complexes.

Compound	λ_{max} / nm (log ε)	Fluorescence max / nm
$[Ru(NCPh)(PPh_3)_2Cp]PF_6$[a]	307 (4.13)	
6	324 (3.89)	
7	315 (3.87)	
$[Ru(NCPh)(dppe)Cp^*]PF_6$[b]	310 (3.74), 346	
10	321 (3.77), 347 sh	
11	309 (3.72), 343 sh	
2	302, 489 (4.15)	620
8	304, 499 (4.33)	619
12	302, 495 (4.29)	616
3	291, 461 (4.18)	576
9	278, 320, 449 (3.90)	581
13	278, 314 sh, 455 (4.02)	578

[a] Ref. [42]. [b] Ref. [37]. sh = shoulder.

Hexaaryl[3]radialene compounds have strong absorption bands between 460-490 nm (figure 3), attributed to the π-π* transition, which account for their intense orange or red colouring. Coordination to ruthenium affects this absorption band slightly with a red shift seen for complexes **8** and **12** (absorption maxima of 495 and 499 nm respectively compared to 486 nm for **2**) and a blue shift seen for complexes **9** and **13** (absorption maxima of 455 and 449 nm respectively compared to 466 nm for **3**). The red shift of complexes **8** and **12** is as expected due to the stabilisation imparted by coordination to the cationic ruthenium species. Furthermore, the *para* substitution of the donor nitrile groups on the propeller-like radialene scaffold positions the coordinated ruthenium metal centre close in space to the nitrile group on an adjacent arm of the radialene which may result in a degree of intramolecular charge transfer. Such interactions have been observed to produce a red shift in extended hexaaryl[3]radialenes with appended triarylamine moieties (λ_{max} ~600 nm) compared to their precursor, hexakis(4-bromophenyl)[3]radialene (λ_{max} 485 nm) [43]. Conversely the blue shifts of complexes **9** and **13** are unexpected. Blue shifts of ligand π-π* transitions are often due to reduced conjugation or a distortion in the ligand structure (*vide infra*). Unfortunately, the aromatic region of ^{1}H NMR spectra of complexes **9** and **13** are too complicated to ascertain whether distortion of the radialene ligand is present.

The free radialenes **2** and **3** also exhibit absorption peaks in the ultraviolet region at 302 and 291 nm respectively. These peaks overlap with the $Ru_{d\pi}$-Cp MLCT and $Ru_{d\pi}$-$NCR_{\pi*}$ MLCT transitions in the absorption spectra of the ruthenium complexes of **2** and **3**, as indicated by a broadening of the peaks although no significant shift in absorption maxima was observed.

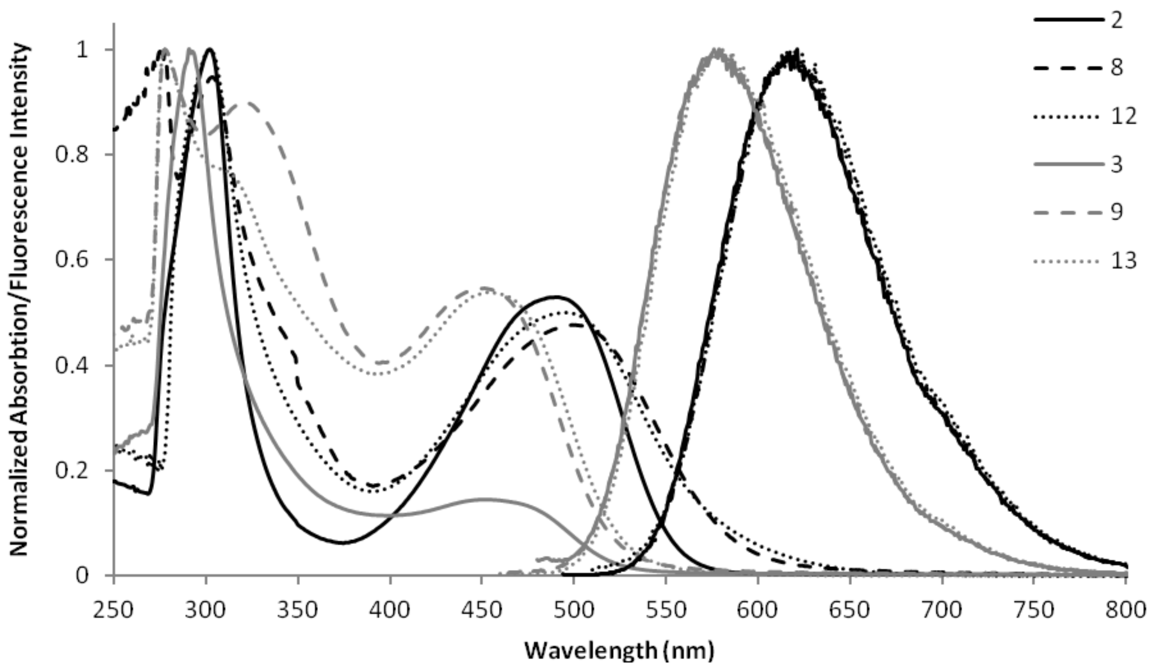

Figure 3. Normalized UV-visible and fluorescence spectra of the hexaaryl[3]radialenes and their ruthenium complexes in dichloromethane (black lines, ligand **2** and its complexes; grey lines, ligand **3** and its complexes). A color version of this image see ESI, Figure S6.

Hexaaryl[3]radialene compounds are also highly fluorescent and exhibit large Stokes shifts of up to 130 nm. Subtle shifts in fluorescence maxima were observed for complexes **8** and **12** (minor decreases from 620 to 619 and 617 nm respectively, compared to **2**) as well as complexes **9** and **13** (slight increases from 576 to 581 and 578 nm respectively, compared to **3**). A red shift is expected, as seen for **9** and **13**, while complexes **8** and **12** show a blue shift. However, in all cases the change in wavelength is only a few nanometres, and given the broadness of the maxima not likely to be particularly significant. The Stokes shifts for the radialene containing complexes are 120, 122, 132, 123 nm for **8**, **12**, **9**, and **13** respectively (compared with 131 and 115 nm for **2** and **3**). The Stokes shifts for complexes **8** and **12** decrease due to the red shift of their respective UV-visible absorption maxima as discussed above, whereas the opposite is observed for complexes **9** and **13**.

Cyclic voltammetry of complexes **6**, **7**, **10** and **11** (Table 4) were performed for 1 mM solutions in dichloromethane containing 0.1 M $[(n\text{-}C_4H_9)_4]NPF_6]$, with potentials referenced against an internal ferrocene standard (Fc/Fc^+ = +0.46 V *vs* SCE). The oxidation potential of ruthenium complexes **6** and **7** was identical at +1.30 V. These oxidation potentials correlate exactly with that of the benzonitrile complex $[Ru(NCPh)(PPh_3)_2Cp]PF_6$ [42] which shows that the extension of the benzonitrile ligand via a methyl spacer has no effect on the electronic properties of the adjacent ruthenium centre. Only one oxidation wave is observed for these complexes confirming that no communication occurs between the metal centres due to the insulating methylene spacer of the dinitrile ligands **4** and **5**. A similar observation is noted for complexes **10** and **11** which exhibit oxidation potentials within the margin of error for the equivalent benzonitrile complex $[Ru(NCPh)(dppe)Cp^*]PF_6$ (+1.10 V) [37]. Again only one oxidation wave was observed. Complexes **8**, **9**, **12** and **13** were not stable in the presence of supporting electrolyte and thus no electrochemical studies were completed.

Table 4. Electrochemical properties of the ruthenium complexes **6**, **7**, **10** and **11**.

Compound	$E_{ox(1)}$[a,b] (V)
$[Ru(NCPh)(PPh_3)_2Cp]PF_6$[c]	+1.30
6	+1.30 (2e$^-$)
7	+1.30 (2e$^-$)
$[Ru(NCPh)(dppe)Cp^*]PF_6$[d]	+1.10
10	+1.08 (2e$^-$)
11	+1.07 (2e$^-$)

[a] Potentials (V) measured in CH_2Cl_2/0.1 mol.L^{-1} $[(n\text{-}C_4H_9)_4]NPF_6$ (in CH_2Cl_2 the ferrocene/ferrocenium couple occurred at +0.46 V vs. Ag/Ag$^+$). [b] Uncertainty in $E_{1/2}$ values *ca.* ± 0.02 V. [c] Ref. [42]. [d] Ref. [37]. sh = shoulder.

4. Conclusion

In summary eight new ruthenium complexes have been synthesised; four of these are dinuclear complexes of diarylmethanes **4** and **5**. Due to synthetic challenges, only mononuclear complexes of radialenes **2** and **3** with $Ru(PPh_3)_2Cp$ and Ru(dppe)Cp* were able to be obtained as single products. An anticipated red shift occurs for the π-π* transition in complexes **8** and **12** (4-cyano derivative) due to the stabilisation imparted by coordination to the ruthenium centre. Surprisingly, a blue shift was observed for complexes **9** and **13**. For the *meta* isomer **3** it is possible that coordination of the bulky ruthenium species is causing a structural distortion or a reduction in conjugation for the ligand structure and hence the blue shift. In terms of electrochemical potentials of the $Ru(PPh_3)_2Cp$ and Ru(dppe)Cp* centres in dinuclear complexes **6**, **7**, **10** and **11**, the diarylmethane ligands **4** and **5** have almost no effect on the redox properties of the metals which display similar oxidation potentials to $[Ru(NCPh)(PPh_3)_2Cp]PF_6$ and $[Ru(NCPh)(dppe)Cp^*]PF_6$ and only one oxidation wave. Unfortunately, the possibility of directly exploring the effect of cross-conjugation in the

[3]radialene series on metal-metal interactions was rendered impossible by difficulties in cleanly isolating targeted dinuclear and trinuclear complexes. Thus, while such multidentate [3]radialene ligands offer interesting opportunities in terms of the electronic properties of high nuclearity complexes, challenges in accessing such species remain.

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